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NOL TECHNICAL REPORT

PHOTOCHEMISTRY OF TNT: INVESTIGATION OF THE "PINK WATER" PROBLEM

BY
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Charles E. Adams

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13. ABSTRACT

Irradiated aqueous solutions of TNT ("pink water") were found to contain numerous organic compounds. Eight photo-decomposition products, amounting to 20% by weight of the photolyzed TNT, have been identified as 1,3,5-trinitrobenzene, 2,4,6-trinitrobenzaldehyde, 4,6-dinitroanthranil, 2,4,6-trinitrobenzonitrile, and four isomers of tetranitroazoxytoluene. Suggestions are put forth on the nature of the 80% photo-decomposition products remaining unidentified in the "pink water" based on the photolysis results of the individual photo-products isolated; i.e., photolysis of 2,4,6-trinitrobenzaldehyde in water rapidly converts to the dibasic acid, 2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene (the "white compound" observed in TNT manufacture). Evidence is also presented on the nature of the primary photolytic process based on deuterium exchange experiments and the measurement of photo-decomposition at various acidities.

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NOLTR 73-172 3 October 1973

PHOTOCHEMISTRY OF TNT: INVESTIGATION OF THE "PINK WATER" PROBLEM

"Pink water" is the visible evidence of the pollution of streams by contaminated waste water from TNT plants. The coloration is formed by the action of sunlight on dissolved TNT. This report identifies the photo-decomposition products of TNT and presents evidence on the photochemical mechanism involved in their formation. Such information is necessary to assess the hazard of such pollution and to devise means to counteract it. The work was funded by the Army's Picatinny Arsenal.

ROBERT WILLIAMSON II

Carl Boyars

CARL BOYARS
By direction

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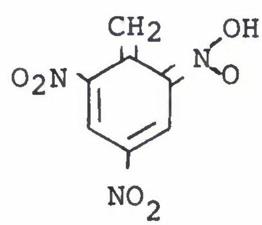
INTRODUCTION

2,4,6-Trinitrotoluene (TNT), both in solution and as a solid, becomes intensely colored when exposed to strong sunlight. Aqueous solutions of TNT, turn pink initially, and over a period of 4 to 6 hours of exposure, gradually darken to yield a cloudy, rusty-orange colored solution, commonly referred to as "pink water". Due to the large volumes of TNT contaminated process water ($>10^6$ gal/plant/day), and the pollution potential of this water when discharged, a knowledge of the composition of "pink water" would be useful in assessing its toxicity and developing possible methods for inhibiting its formation.

A survey of the literature for references to the photolysis of TNT, produced an early report[1] of the separation of 2-nitroso-4,6-dinitrobenzyl alcohol from photolyzed solid TNT. However, later workers[2] could not reproduce these results. More recently, Sandus and Slagg[3], found that flash photolyzed solutions of TNT contained a short lived species, λ_{max} = 470 nm, for which the structure 7 the aci form of TNT, was proposed.



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1 Shultz, G. and Ganguly, K. L., Ber. 58, 702 (1925).
2 Gray, D. N. Bonomo, F. S., and Denner, R. I., "Study on the effect of temperature cycling of high explosives", Report AFSWC-TDR 62-16. Contract No. AF 29 (601) 2771, March 1962.
3 Sandus, O. and Slagg, N., "Reactions of Aromatic Nitrocompounds. I Photochemistry", TR 4385 Picatinny Arsenal (1972).

A similar proposal for the primary photolytic process for flash photolyzed solutions of 2,6-dinitrotoluene was made previously by Wettermark[4].

Sandus and Slagg[3] also observed that the quantum yields for the disappearance of TNT as well as other mono and dinitrotoluenes were exceedingly small. This small value, $\sim 10^{-3}$, for the quantum yield suggested that the primary photo-products might also be photochemically unstable. These data suggest that "pink water" would contain a rather complex mixture of nitrobodies. Extrapolation of the results obtained from the study of the products formed on decomposing TNT by a thermal process[5] tend to support this conclusion.

We, therefore, attacked the "pink water" problem with a manifold approach in this preliminary investigation. First, it was decided to attempt to separate and identify those compounds which were obtained in a benzene extract of "pink water". It was expected that these would be "one-ring" compounds more nearly related to the primary photo-process. Secondly, we initiated studies such as photo-deuterium exchange at various acidities, the effect of solvent on the composition of the photo-products and photostability of separated photo-products to enable us to better understand the nature of some of the photochemical and non-photochemical processes taking place in "pink water" formation. This report presents the results of these preliminary studies. These results in turn, suggest several avenues of investigation to be followed in our subsequent work.

EXPERIMENTAL

Photolysis Apparatus

Irradiation of aqueous TNT solutions in the laboratory was performed with a 450 watt Hanovia medium pressure mercury arc lamp, fitted with a pyrex filter #7740. To a first approximation, this apparatus duplicated solar radiation, but with greater intensity and reliability. The medium pressure mercury arc radiates a broad spectrum from the far UV (2000Å) to the infra-red region[6]. Placing a

4 Wettermark, G., M. E. Langmuir, L. Doglotti, E. D. Black, JACS. 91 2204 (1969).
5 J. C. Dacons, H. G. Adolph, and M. J. Kamlet, J. Phys. Chem., 74, 3035 (1970).
6 J. C. Calvert and J. N. Pitts Jr., Eds., "Photochemistry" J. Wiley and Sons (1967).

pyrex filter (#7740) between the arc and the TNT solution allowed only light above 2800 Å to pass into the TNT solution. By comparison, the earth's atmosphere absorbs virtually 99% of the radiation below 2800 Å emitted by the sun[7]. Additional evidence for the similarity of the solar and laboratory sources was obtained from a close similarity of the TLC plates of the benzene extracts obtained from solar irradiated and Hg-vapor lamp irradiated TNT solutions.

The photochemical reaction vessel consisted of a 500 ml (Ace Glass #6515) reactor fitted with a quartz immersion well (Ace Glass #6515-27) containing a cooling jacket. The pyrex filter and mercury lamp were placed inside the well.

Preparation of Aqueous TNT Solutions

Production grade TNT was recrystallized twice from carbon tetrachloride (Darco G-60). The TNT obtained is of high purity (99.9%), as confirmed by TLC (2-dimensional) using ethylene diamine - dimethylsulfoxide (EDA/DMSO) spray reagent[8] and gas chromatography.

An efficient method was developed whereby saturated solutions of TNT in water (120 to 130 ppm at room temperature) were obtained by simply allowing distilled water to pass through a one inch diameter glass column packed with 75 to 100 g TNT. Using this technique with a water pump vacuum on the column take-off, four liters of saturated TNT solution can be obtained in 45 minutes.

In order to obtain larger concentrations of photo-products than possible by photolyzing room temperature saturated solutions (~ 130 ppm TNT), a continuous flow system was designed to continuously prepare and photolyze TNT solutions at elevated temperatures. Using a TNT packed column as described above with gravity flow (7 to 10 ml/min) rather than vacuum assisted water flow, the column was heated to 60°C by means of an exterior heating tape after charging it with water from a constant level gravity feed reservoir. The hot effluent, 600 ppm TNT, was fed directly into the cooling chamber section of the quartz immersion well (Figure 1) where it was irradiated with the medium pressure mercury lamp. The temperature of the photo-reaction mixture in the cooling chamber was maintained at 50 - 60°C by keeping a proper balance between the heat from the Hg—lamp and the cooling water circulating through the outer jacket. At flow rates of 7 to 10 ml/min of the 600 ppm TNT solution through this apparatus, 60 to 70% of the TNT was photo-decomposed during its residence time in the reactor.

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7 L. R. Kollar, "Ultraviolet Radiation", 2nd Ed., J. Wiley and Sons (1967).

8 J. C. Hoffsommer and J. F. McCullough, J. Chromatog., 38, 508 (1968).

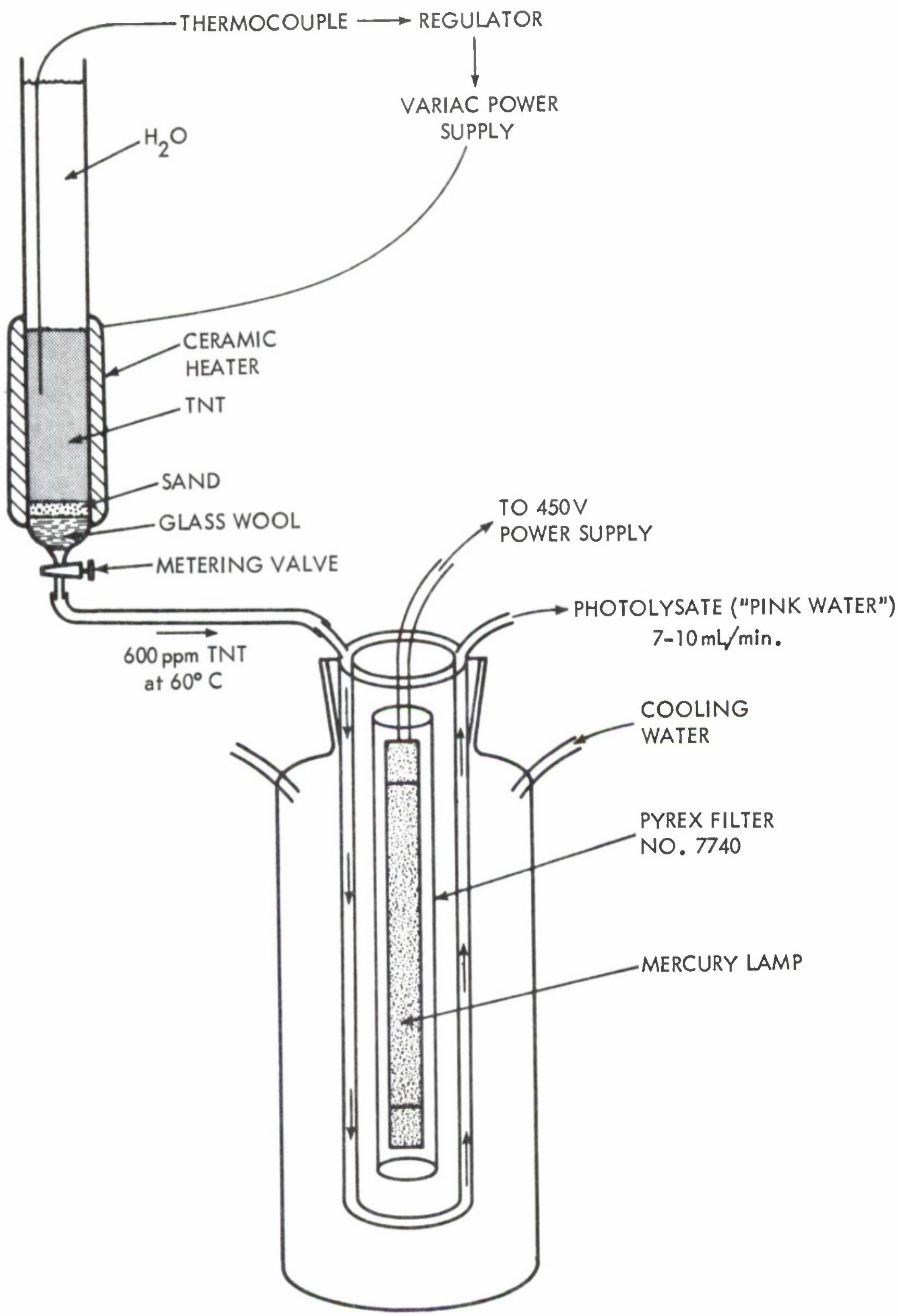

FIG. 1 PHOTOCHEMICAL REACTION VESSEL

TNT Analysis

The concentrations of TNT, before and after photolysis, were determined by gas chromatography. Quantitative benzene extractions of the aqueous solutions were analyzed after adding dimethoxytrinitrobenzene as an internal standard. Microliter samples of these benzene solutions were assayed using a Hewlett Packard 5750 gas chromatograph, equipped with a dual column, electron capture detector unit, and an Infotronics automatic digital integrator. The gas chromatography column support was 3% Dexsil 300 on Chrom. W: AW-DMAC 80/100.

Thin Layer Chromatographic Analysis

Thin layer chromatographic plates were prepared according to the method of Hoffsommer[8] using Brinkman Silica gel HF 254 as the adsorbent. As purchased, it contains a fluorescent indicator which allows location of the developed spots with 2540 Å light. These plates were used exclusively for identification of products in the benzene soluble portion of the photolysate. All TLC plates were developed with benzene. Visualization of spots on the developed TLC plate was accomplished with EDA/DMSO spray reagent[8]. Polynitroaromatic compounds give intense, brightly colored "Meisenheimer" type complexes with this reagent[9].

RESULTS

Benzene Extract of "Pink Water"

Utilizing the continuous feed photolysis apparatus described previously, 17.5 liters of TNT solution (600 ppm) were photolyzed at ~60°C. Analysis of the photolysate for TNT by gas chromatography showed that 65% TNT has been photolyzed. Preliminary separation of the photo-products was obtained by extraction of the aqueous reaction mixture with benzene. Upon removal of the benzene the residue accounted for 20% of the photo-decomposition products in addition to the unreacted TNT. The residue was analyzed by TLC and the products separated by column chromatography. The isolated products were characterized by NMR, IR, and MS, (and final identification was achieved by comparison with the known compounds). Table I lists the compounds along with their R_f values, color of TLC spot with EDA/DMSO spray reagent, and the approximate percent yield based on the weight of TNT decomposed.

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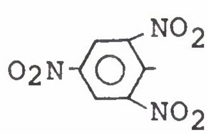
9 D. J. Glover and L. Kayser, Anal. Chem. 40 2055 (1968).

TABLE I

Compound	R_f value[a]	Color[b]	% Yield
TNT	0.85	dark brown	---
1,3,5-Trinitrobenzene (TNB)	0.80	orange-brown	0.5-1.0
4,6-Dinitroanthranil (Anil)[c]	0.55	pink-red	3-4
2,4,6-Trinitrobenzaldehyde(PiCHO)[d,e]	0.51	red	8-10
2,4,6-Trinitrobenzonitrile (PiCN)[f]	0.42	brown	3-4

a) Developing solvent - benzene
b) With EDA/DMSO reagent
c) Can be prepared by the method of J. S. Splitter and M. Calvin (J. Org. Chem., 20, 1086 (1965))

d) Pi =



e) Obtained from Aldrich Chem. Co. and recrystalized from benzene (Darco 60).
f) Can be prepared by the action of copper cyanide on picryl chloride (J. Konarski and A. Graczyk, Roczniki Chemii 46, 745 (1972)).

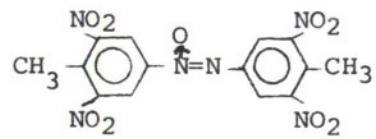
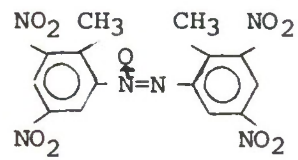
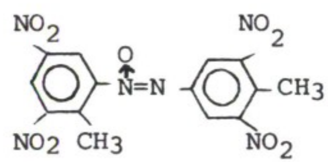
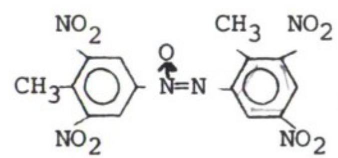
In a second experiment, an aqueous TNT solution, in a quartz flask at room temperature (120 ppm), was allowed to stand in sunlight for four days (approximately 30 hrs sunlight). After this time, G. C. analysis showed 75% of the TNT had photolytically decomposed. Examination of the benzene extracts of this photolysate by TLC revealed several new compounds in addition to those found when the mercury lamp was used (vida supra). These new spots on the TLC plate produced blue and purple colors when sprayed with EDA/DMSO. The colors suggested "azoxy" type compounds similar to those previously synthesized in this laboratory[10].

10 M. E. Sitzmann, NOLTR 73-70 "Chemical Reduction of TNT - Initial Products" 1973.

Comparing the R_f values and colors of the four known "azoxy" derivatives of TNT[10] with the TLC spots from sunlight irradiation of TNT confirmed their identity. Table II lists the "azoxy" photo-products. These apparent photo-reduction products of TNT occur only in trace amounts (≈1%) in "pink water".

TABLE II

R_f Values and EDA/DMSO Spot Color of Tetranitroazoxytoluenes

Compound	Structure	R_f[a]	Color[b]
2,2',6,6'-tetranitro-4,4'-azoxytoluene (2)		0.75	blue
4,4',6,6'-tetranitro-2,2'-azoxytoluene (3)		0.45	blue
2',4-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene (4)		0.55	purple
2,4'-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene (5)		0.55	purple

a) benzene solvent

b) EDA/DMSO reagent

Attempted Separation of the Non-Benzene Soluble Photo-decomposition Products

Only 20% of the "pink water" products were extractable into benzene and identified. The remaining 80%, in the water phase, has so far defied separation.

Extraction of the aqueous phase with nitromethane transferred about half of the remaining organics to the organic phase. Numerous attempts at thin layer chromatography on silica gel, kieselguhr and polyamide support phases with a variety of solvents failed to give any usable separations of the nitromethane extracts. Numerous compounds appeared to be present.

Following the nitromethane extraction, the water layer, now containing ~40% of the total photo-decomposition products, was not further extractable with the usual water immiscible organic solvents. However, after acidification of the water layer to pH = 1, extraction of all of the decomposition products was achieved with diethyl ether. Furthermore, the color of the water layer changed, upon acidification, from rusty-orange to light yellow. This suggested protonation of the colored anions of strongly acidic species was taking place. The acidic nature of the compounds in the ether extract also suggested a chromatographic separation using a weakly polar polymaide support phase (Nygel and Machery-Nylon 6). Attempts to chromatograph the solids from the ether extract, loaded onto a dry packed polyamide column with dimethylformamide or glacial acetic showed some diffuse and overlaping bands but no pure compounds could be obtained. This adsorbent appears to be promising and will be investigated further.

Photolysis of TNT in Other Solvent Systems

From the photochemical results obtained in the aqueous system, it appeared that TNT could act as both a hydrogen donor, the conversion to such products as 2,4,6-trinitrobenzaldehyde, as well as a hydrogen acceptor in forming polynitroazoxytoluenes. As a consequence, it could be assumed that a primary photo-produced intermediate was entering into a bimolecular reaction with either ground state or excited TNT. To attempt to reduce the number of secondary reactions taking place in the aqueous system, we initiated a preliminary investigation of the photolysis of TNT in solvents which we believed could act as hydrogen donor or acceptor molecules. When carried out in methanol, the rate of photo-decomposition is markedly reduced. However, TLC showed that the benzene soluble products are essentially the same as those formed in water. Using cyclohexane as solvent, TNT disappeared at about the same rate as in water. However, TLC showed that none of the products corresponded to those formed in the aqueous system. This system will be investigated further.

The search for a hydrogen donor solvent, superior to the methyl group of TNT, ended when the photolysis was run in tetrahydrofuran. In this solvent, a 47% yield of the four isomeric tetranitroazoxytoluenes (Table II) was obtained. NMR analysis of the mixture as well as gravimetric analysis of the fractions collected from the column chromatographic separation of this mixture were the same with the following percentages of products obtained; 2 (18%), 3 (9.5%), 4 + 5 (18.5%). The high degree of structural similarity between 4 and 5 prevented the determination of their individual yields.

Similar products were obtained when dioxane was substituted for tetrahydrofuran as a reaction solvent. In dioxane-d_8, we further observed, that the TNT recovered from the photolysate had not exchanged hydrogen for deuterium at either the methyl or ring carbon atoms. These results indicated that the aci-form 1 may not be an intermediate in the photo-transformation of TNT to the tetranitroazoxytoluenes. A mechanism involving transfer of hydrogen from solvent to a nitro group of TNT to form nitroso and/or hydroxylamino derivatives which subsequently dimerize to form the azoxy-function[11] may be operating in these ether solvents.

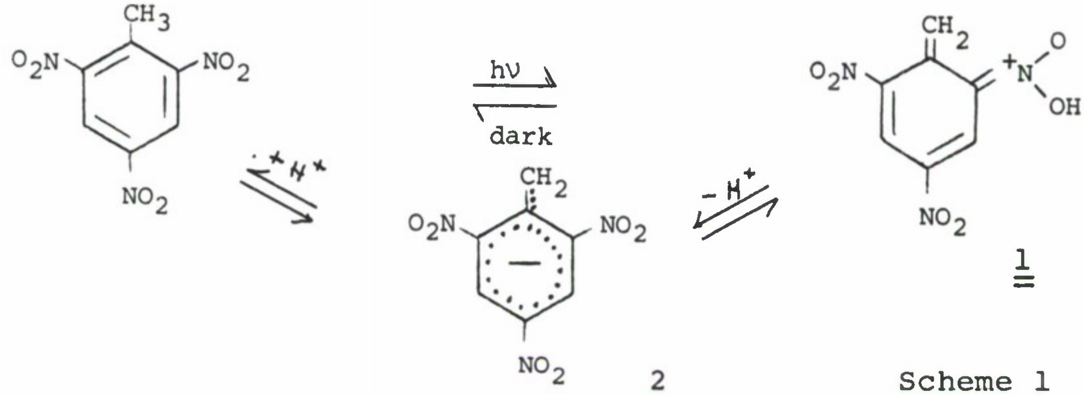
It is possible that intermolecular hydrogen transfer between a methyl group of one TNT molecule and the nitro group of a second TNT molecule can also occur in the aqueous system. The donor TNT molecule would be oxidized, i.e., products such as 2,4,6-trinitrobenzaldehyde, and the acceptor molecule reduced as in the ether solvents. The cyclic ether solvents, being better hydrogen donors[12] than the methyl group of TNT, appear to direct the reaction to form high yields of reduced nitro derivatives; i.e., the tetranitroazoxytoluenes. We are currently seeking hydrogen acceptor solvents which will yield oxidized methyl group but not reduced nitro group photo-products.

Effect of Acidity on the Photo-Decomposition of TNT

Extrapolating the results of studies[4] of the flash photolysis of 2,6-dinitrotoluene to TNT suggests the following mechanism (Scheme 1) for the primary photochemical step in the photo-decomposition of TNT.

11 P. A. S. Smith, Ed., "Open-Chain Nitrogen Compounds" Vol. II W. A. Benjamin Inc. New York 1966 p. (367).

12 THF is known to give ESR signals when photolyzed in nitromethane; R. L. Ward, J. Chem. Phys., 32 2588 (1965).



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Scheme 1

Irradiation of TNT produces an excited state which is converted to the aci-form 1 by intramolecular hydrogen transfer[13]. Subsequent ionization of the aci-form 1 produces the anion 2 which can either reprotonate to form TNT or undergo decomposition to the observed photo-products.

To test the possibility of a labile hydrogen being transferred in the primary photo-step and to distinguish between the anion 2 or the aci-form 1 as the precursor of at least one of the TNT photo-decomposition paths, we designed some preliminary experiments to determine whether the rates of photo-decomposition of TNT and deuterium exchange were comparable. These results are summarized in Table III.

TABLE III

Photo-decomposition of TNT in D_2O

pH	$[TNT]_0^a$	$[TNT]_{60}^{a,b}$	%D[c]	% Decomp.
1.1[d]	119	115	75	3
3.0[e]	135	71	--	48
6.0[f]	126	39	50	70

13 In this discussion, our preliminary data do not permit us to decide whether the aci-form 1 or the anion 2 are either excited or ground states. The possibility exists that the aci-form 1 may return to the ground state prior to ionization. Still another possibility is that irradiation of TNT produces an excited TNT molecule which subsequently forms either the excited aci-form by intramolecular hydrogen transfer or the anion 2 by loss of a proton. We plan to investigate these transformations in greater detail.

a) Concentrations in ppm.
b) After 60 minutes irradiation.
c) Deuterium incorporation at the TNT methyl group was determined by mass spectrometric comparison of the 210/211 peak ratios "normal" TNT with the TNT recovered after irradiation in D_2O. Control samples of TNT in D_2O at pH = 1.1 and 6.0 neither exchanged H for D nor underwent decomposition when kept in the dark for the same length of time.
d) Adjusted to pH 1.1 with D_2SO_4.
e) This run carried out in H_2O/H_2SO_4.
f) No added acid.

Inspection of the data in Table III shows an inverse relationship between the photo-decomposition of and the deuterium uptake by TNT. If scheme 1 is the primary photochemical sequence as suggested by Wettermark[4] and also indicated by the results of Slagg and Sandus[3], then an increase in deuterium exchange is expected at higher acidity where the rate of recombination of anion 2 with a deuteron would be greater. However, the photo-decomposition rate decreases markedly as the acidity increases. This indicates that the anion 2 and not the aci-form 1, is involved in the photo-decomposition of TNT. It would be expected that the concentration of the anion would be proportionally larger at higher pH values where the rate of photo-decomposition is markedly increased.

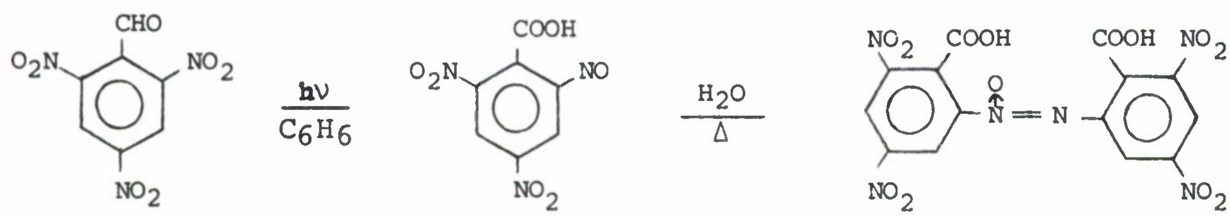
Photolysis of Isolated "Pink Water" Products

When an aqueous solution of 2,4,6-trinitrobenzaldehyde (400 ppm) was photolyzed with the Hg-arc, the concentration of the aldehyde was reduced to 1 ppm after 12 minutes. From the acidified photolysate, we obtained a white solid, m. 245° dec., which exhibited acidic properties.

Literature reports[14] that the photolysis of 2,4,6-trinitrobenzaldehyde affords quantitative yields of 2-nitroso-4,6-dinitrobenzoic acid, 6. Though 6 would exhibit the observed acidic properties, it is a green solid, m. 200.5°. However, 6 is rapidly converted to the dibasic acid 7, m. 245° dec., on warming in aqueous solution[14]. Repetition of this work[14] showed that 7 was identical with the white compound, m. 245° dec, isolated from the photolysis of an aqueous solution of 2,4,6-trinitrobenzaldehyde[15]. These results indicate that

14 S. A. Joshi and W. D. Patwardhan, Current Science, 8, 239 (1953).
15 The azoxy derivative 7 is identical with the "white compound" formed as a by-product in the continuous production of TNT.

one of the components, perhaps a major one in view of the relatively large yield of 2,4,6-trinitrobenzaldehyde (Table I), of the water soluble (benzene insoluble) fraction is the azoxy derivative 7.



6 7

In a similar fashion, an aqueous solution (100 ppm) of 4,6-dinitroanthranil was photolyzed and during the reaction an orange solid separated. Recrystallization from benzene gave dark orange crystals which turned tan at 140° and decomposed with gas evolution at 170°. Its spectrum indicated a molecular weight of 418; twice the molecular weight of the anil. The presence of a very intense P-44 mass peak, suggests a loss of carbon dioxide which would be indicative of a carboxyl function. Its structure is still under investigation. The interesting point is that only one compound arises from the photolysis of the anil and this compound is acidic and very insoluble in water. Solid also separates out during irradiation of aqueous TNT solutions.

The photolysis of 1,3,5-trinitrobenzene (Table I) in aqueous solution did not produce any photo-products after 6 hours of irradiation by the Hg-arc. Gas chromatographic assay of the solution after irradiation showed no change in the concentration of 1,3,5-trinitrobenzene. The photolysis of other products isolated from the photolysis of aqueous TNT solutions is currently under investigation.

ACKNOWLEDGMENTS

The authors are very grateful to Donald J. Glover for TNT analyses and to Dr. Donald Kubose for mass spectral analyses, Miss Eleonore G. Kayser for determination of NMR spectra, and Mr. David Ludwig for his technical assistance.

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